

CLAIMS

1. Method for selective separation by density of each constituent of a mix of organic synthetic materials and particularly comminuted waste materials to be reused by recycling, stable within a precision level of  $\pm 0.0005$  about a density level "ds" chosen as the density separation threshold equal to at least 1, and consisting of separating them by density difference, in an aqueous suspension of an appropriate quantity of powder particles dispersed in a sufficient quantity to create the density level "ds" chosen as the separation threshold of at least one of the constituents of the mix of fragmented synthetic organic materials to be selectively separated, characterised in that the separative suspension is formed from:
- 10           a) solid powder particles with a size grading cutoff not more than 30  $\mu\text{m}$ , these solid powder particles thus sized being dispersed in the aqueous phase in a sufficient quantity to reach the chosen density threshold "ds",
- b) a water soluble stabiliser to stabilise the rheological and invariance characteristics of the density "ds" with a precision of the said density "ds"
- 15           of the suspension of solid powder particles equal to  $\pm 0.0005$ .
2. Method according to claim 1, characterised in that the solid powder particles preferably have a size grading cut-off not more than 20  $\mu\text{m}$  and even better not more than 5  $\mu\text{m}$ , these solid powder particles thus sized being dispersed in the aqueous phase in a sufficient quantity to create the chosen density threshold "ds".
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3. Method according to claim 1 or 2, characterised in that the powder particles are of natural origin and chosen from the group of powder mineral materials consisting of clays, belonging to families consisting of the group composed of kaolinites, comprising kaolinite, dickite, halloysite, disordered kaolinites, serpentines, the micas group and particularly muscovite, biotite, paragonite, pyrophyllite and talc, illites and glauconite, the montmorillonites group and particularly beidellite, stevensite, saponite, hectorite; the chlorites group; the vermiculites group; the interstratified clays group for which the unit structure is a combination of the previous groups; the fibrous clays group, and particularly attapulgite (palygorskite), sepiolite; the group
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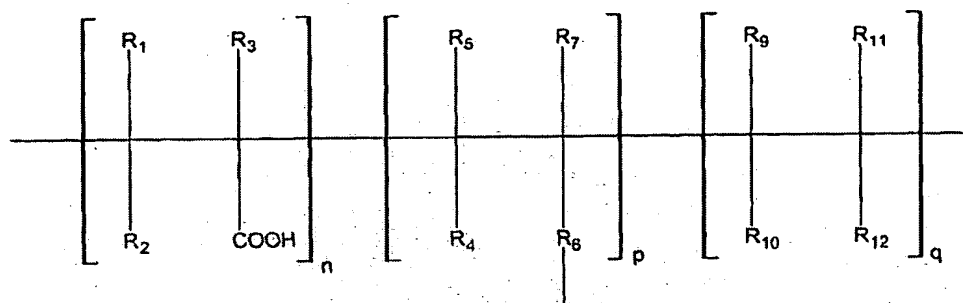
consisting of calcium carbonate (calcite), magnesium carbonate, dolomite (double calcium and magnesium carbonate), dehydrated calcium sulphate (gypsum), barium sulphate, talc, alumina, silica, titanium dioxide, zirconia, taken alone or mixed.

5 4. Method according to claim 1 or 2, characterised in that the powder particles are of synthetic origin and are chosen from among the group consisting of glass powders, precipitated calcium carbonate, metallic powders, taken alone or mixed.

10 5. Method according to at least one of claims 1 to 4, characterised in that the median diametric dimension of the powder particles is limited to 5  $\mu\text{m}$  and preferably between 1  $\mu\text{m}$  and 0.005  $\mu\text{m}$ .

15 6. Method according to one of claims 1 to 5, characterised in that the water soluble agent for stabilisation of rheological characteristics and to maintain the apparent density "ds" of the suspension of solid powder particles, is chosen from the group composed of phosphates and polyphosphates, alkylphosphate esters, alkylphosphonate, alkylsulfate, alkylsulfonate esters, lignin, liginosulfonates in the form of calcium, sodium, iron, chromium, iron and chromium salts, copolymers of maleic anhydride and sulfonic styrene acid, substituted, neutralised, esterified or non-  
20 esterified copolymers of methylacrylamide and (methyl) acrylic acid, copolymers of sulfonic methylacrylamido-alkyl acid and (methyl) acrylamide acid, water soluble polymers of acrylic acid used in acid form of possibly wholly or partly neutralised by alkaline and/or alkali earth agents, by amines salified by single-valent and/or polyvalent ions, and/or esterified, or by water soluble acrylic copolymers with  
25 phosphated, phosphonated, sulphated or sulfonated functions.

7. Method according to claim 6, characterised in that the water soluble agent is preferably chosen from among water soluble acrylic copolymers satisfying the general formula:



in which:

- ✓  $Z$  is a phosphate, phosphonate, sulphate, sulfonate type pattern with at least one free acid function,
- 5 ✓  $n$  is equal to a value of between 0 and 95,
- ✓  $p$  is equal to a value of between 95 and 5,
- ✓  $q$  is equal to a value of between 0 and 95,
- ✓ the total value of  $n + p + q$  is equal to 100,
- ✓  $R_1$  and  $R_2$  are hydrogen simultaneously, or one is hydrogen while the other is a carboxylic function that may or may not be esterified by an alcohol in  $C_1$  to  $C_{12}$ ,
- 10 ✓  $R_3$  is hydrogen or an alkyl radical in  $C_1$  to  $C_{12}$ ,
- ✓  $R_4$  and  $R_5$  are simultaneously or separately hydrogen or an alkyl radical in  $C_1$  to  $C_{12}$ , a substituted or non-substituted aryl, a carboxylic function that may or may not be esterified by an alcohol in  $C_1$  to  $C_{12}$ ,
- 15 ✓  $R_6$  is a radical that sets up the link between the pattern  $Z$  and the polymeric chain, this radical  $R_6$  possibly being an alkylene with formula  $CH_{2r}$  in which  $r$  may be equal to values in the interval 1 to 12, an oxide or polyoxide of alkylene with formula  $R_8O_s$  in which  $R_8$  is an alkylene in  $C_1$  to  $C_4$  and  $s$  may be any value from 1 to 30, or a combination of the two formulas  $CH_{2r}$  and  $R_8O_s$ ,
- 20 ✓  $R_7$  can be hydrogen or an alkyl radical in  $C_1$  to  $C_{12}$ ,
- ✓  $R_9$  and  $R_{10}$  are simultaneously hydrogen, or one is hydrogen and the other is a carboxylic group, an ester in  $C_1$  to  $C_{12}$ , an alkyl in  $C_1$  to  $C_{12}$ , an aryl in  $C_5$  or  $C_6$  or an alkylaryl,
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✓  $R_{11}$  may be hydrogen, a carboxylic group, an alkyl in  $C_1$  to  $C_3$  or a halogen,

5 ✓  $R_{12}$  may be an ester in  $C_1$  to  $C_{12}$ , a substituted or non-substituted amide, an alkyl in  $C_1$  to  $C_{12}$ , an aryl in  $C_5$  or  $C_6$ , an alkylaryl, a halogen, a carboxylic group or an alkyl or aryl phosphated, phosphonated, sulphated, sulfonated group.

8. Method according to claim 7, characterised in that in pattern Z, the non-free acid functions are occupied by a cation, an ammonium group, an amine, an alkyl in  $C_1$  to  $C_3$ , an aryl in  $C_3$  to  $C_6$  substituted or not, an alkylaryl, an ester in  $C_1$  to  $C_{12}$  and preferably in  $C_1$  to  $C_3$ , or a substituted amide.

9. Method according to claim 8, characterised in that the total value of  $n + p + q$ ,  $n = 0$ , when  $q > 0$  and  $q = 0$  when  $n > 0$ .

15 10. Method according to claim 8, characterised in that, in patterns  $R_1$  and  $R_2$ , the alcohol esterifying the carboxylic function is preferably  $C_1$  to  $C_4$ .

20 11. Method according to claim 9, characterised in that, in pattern  $R_3$ , the alkyl radical is preferably in  $C_1$  to  $C_4$ .

12. Method according to claim 8, characterised in that, in patterns  $R_4$  and  $R_5$ , the alkyl radical is preferably in  $C_1$  to  $C_4$ .

25 13. Method according to claim 8, characterised in that, in patterns  $R_4$  and  $R_5$ , the alcohol esterifying the carboxylic function is preferably in  $C_1$  to  $C_4$ .

14. Method according to claim 8, characterised in that, in pattern  $R_7$ , the alkyl radical is preferably in  $C_1$  to  $C_4$ .

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15. Method according to claim 8, characterised in that, in patterns  $R_5$  and  $R_{10}$ , the ester is preferably in  $C_1$  to  $C_3$ .
16. Method according to claim 7, characterised in that, in patterns  $R_9$  and  $R_{10}$ , the  
5 alkyl is preferably in  $C_1$  to  $C_3$ .
17. Method according to claim 7, characterised in that, in pattern  $R_{12}$ , the ester is preferably in  $C_1$  to  $C_5$ .
- 10 18. Method according to claim 7, characterised in that, in pattern  $R_{12}$ , the alkyl is preferably in  $C_1$  to  $C_3$ .
19. Method according to claim 7, characterised in that the molecular mass of water  
15 soluble acrylic copolymers forming the stabilisation agent is between 5000 and 100 000.
20. Method according to claim 7, characterised in that the water soluble acrylic copolymers forming the stabilisation agent are at least partially neutralised, using a neutralisation agent chosen from the group composed of sodium, potassium,  
20 ammonium, calcium, magnesium hydroxides, and primary, secondary or tertiary, aliphatic and / or cyclic amines such as mono, di, tri ethanolamines, mono and diethylamines, cyclohexylamine, methylcyclohexylamine, etc.
21. Method according to at least one of claims 1 to 20, characterised in that the  
25 quantity by weight of the water soluble stabilisation agent is expressed as the dry weight of the said agent as a percentage of the dry weight of powder particles put in suspension, and is between 0.02% and 5%, and preferably between 0.1% and 2% dry weight of the dry weight of the powder particles.
- 30 22. Method according to at least one of claims 1 to 21, characterised in that the aqueous phase has a conductivity of not more than 50 ms, and preferably between 0.2 ms and 40 ms.

23. Method according to at least one of claims 1 to 22, characterised in that it is carried out in at least one hydraulic separator.

5 24. Method according to claim 23, characterised in that, when the said method is carried out in a single hydraulic separator, the chosen density "ds" varies:

- in increasing order, by controlled addition of the defined powder particles and the water soluble stabilisation agent in the suspension present in the said hydraulic separator, until the new chosen threshold density "ds" is obtained,
- 10 - in decreasing order, by adding water until obtaining the new chosen threshold density "ds".

25. Method according to claim 24, characterised in that the density of the separative stable suspension is varied, to increase it or to decrease it, while maintaining mechanical stirring of the dense aqueous medium being corrected and / or while recirculating the dense medium by drawing off from the bottom of the hydraulic separator and reinjection at the top of the said separator.

20 26. Method according to claim 23, characterised in that if the said method is performed in several hydraulic separators, the various separators are placed one after the other, using a cascade system operating with stable suspensions each having a precise density threshold "ds", in an increasing or decreasing order of the densities.

25 27. Method according to any one of claims 23 to 26, characterised in that the threshold density "ds" of the precise aqueous separative suspension is continuously controlled by appropriate measurement means and is corrected as soon as a drift is detected.

30 28. Method according to claim 27, characterised in that the density of the dense medium contained in each hydraulic separator is controlled using two solenoid valves each opening onto two circuits connected to two reservoirs, one of the

reservoirs containing a concentrated "mother" suspension of powder particles, stabilised with a water soluble stabilisation agent so that a determined quantity of the mother suspension can be added to make an upward correction to any downward drift in the density of the dense precise separation medium, the other tank containing  
5 water so that a determined quantity of water can be added to make a downward correction to any upward drift in the density of the dense precise separation medium.

29. Method according to claim 28, characterised in that the density of the dense medium in each hydraulic separator is measured continuously by appropriate  
10 measurement instruments that trigger opening of one of the solenoid valves and then close it when the threshold density "ds" is reached.

30. Method according to any one of claims 23 to 29, characterised in that each suspension may be recirculated in each hydraulic separator by drawing off the said  
15 suspension at the bottom of the said separator and reinjecting it into the upper part.

31. Use of the method according to at least one of claims 1 to 30, for selectively separating mixed polymer materials, and particularly waste materials originating from the destruction of cars and /or durable consumer products at the end of their  
20 lives.